Photocrystallographic Identification of Metastable Nitrito Linkage Isomers in a Series of Nickel(II) Complexes

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Single crystal photocrystallographic experiments and solid state Raman spectroscopy have been used to determine the low temperature, metastable structures of the nickel(II) nitrito complexes $[Ni(aep)_2(\eta^1\text{-}ONO)_2]$ **1†O** (aep = 1-(2-aminoethyl)piperidine), $[Ni(aem)_2(\eta^1\text{-}ONO)_2]$ **2†O** (aem = 1-(2-aminoethyl)morpholine), and $[Ni(aepy)_2(\eta^1\text{-}ONO)_2]$ **3†O** (aepy = 1-(2-aminoethyl)pyrrolidine and where the $^{\dagger O}$ denotes the oxygen-bound nitrito metastable molecule). These linkage isomers of the equivalent nitro complexes $[Ni(aep)_2(\eta^1\text{-}NO_2)_2]$ **1**, $[Ni(aem)_2(\eta^1\text{-}NO_2)_2]$ **2** and $[Ni(aepy)_2(\eta^1\text{-}NO_2)_2]$ **3** are formed by LED irradiation at temperatures below 120 K. The behavior of the three complexes upon irradiation is generally similar, but some subtle differences have been observed. From the crystallographic studies all three complexes **1-3** exhibit the *endo*-nitrito linkage isomer upon irradiation, however, for **3*** (a crystal structure that contains components of both **3** and **3†O**) an *exo*-nitrito isomer is also observed. Under conditions of 90-100 K, with blue light, the conversion percentages to the nitrito isomers, **1†O**, **2†O** and **3†O** were 16 %, 22 % and 30 %, respectively. At temperatures below 110 K all three nitrito isomers were stable for over four hours but while **2†O** and **3†O** could be detected at temperatures down to 30 K, at temperatures below 60 K the metastable structure **1†O** appeared to be quenched and only the nitro isomer **1** was identified in the crystal. The solid state Raman spectra for **1†, 2†** and **3†** confirmed the photocrystallographic results with the nitrito isomers being identified from the O-N-O deformation vibrations.

Introduction

Photocrystallography is a rapidly developing technique, which involves the photo-activation of species within a crystalline lattice, that is bringing a dynamic aspect to X-ray crystallographic experiments, so that reactions within a crystal can be monitored as they occur or the structures of molecules in metastable or short-lived photo-activated states can be determined.[1] Within the area of inorganic and molecular chemistry the technique has been applied to the investigation of solid state reactions,[2] the study of phase transitions[3] and the structural changes resulting from light-induced excited spin-state trapping (LIESST) experiments in spin crossover systems,[4] the investigation of solid state photomagnetic switching,[5] and the structure determination of transient molecular species in three dimensional networks.[6] One of the most promising developments in the field of photocrystallography has been the research involving the full three-dimensional structure determination of metastable and short-lived photo-activated species using single crystal crystallographic techniques with monochromatic X-ray radiation from either a laboratory or synchrotron source. The research area has been pioneered by Coppens who has determined the structures of a range of metastable linkage isomers of transition metal nitrosyl,[7] nitrite[8] and sulfur dioxide[9] complexes in which these ligands adopt uncommon coordination modes. Then, using a pump-probe technique that requires a pulsed laser (the pump) to be synchronized with the mechanically "chopped" X-ray beam from a synchrotron X-ray source (the probe),[10] Coppens and others have gone on to determine the short-lived excited state structures of several bi- and trinuclear transition metal complexes in which there is a significant change in metal-metal distance.[11] Other short-lived geometry changes have also been identified photocrystallographically. For example, the copper(I) cation, $[Cu(dmp)(dppe)]^+$, (dmp = 2,10-dimethylphenroline; dppe = 1,2-bis(diphenylphosphino)ethane), as the crystalline $[PF_6]^-$ salt, shows a significant change towards a more flattened geometry upon excitation by 50 ns pulses of a 355 nm laser at 16 K.[12]

During the last few years we have also been exploring the photocrystallographic method and have established the structure of a second metastable linkage isomer of the $[Ru(NH_3)_4(H_2O)(SO_2)]^{2+}$ cation in which the SO_2 group is η^1-*O*-SO bound.[13] This isomer is generated when single crystals of the complex are irradiated with light from a 200 W tungsten lamp at temperatures below 120 K although the maximum percentage conversion of this isomer, 36 %, occurs at temperatures below 25 K. From our work and that of others it is clear that if solid state metastable systems are to find any applications, as has been suggested recently,[14] reliable 100 % conversion from the thermodynamic ground state structure to

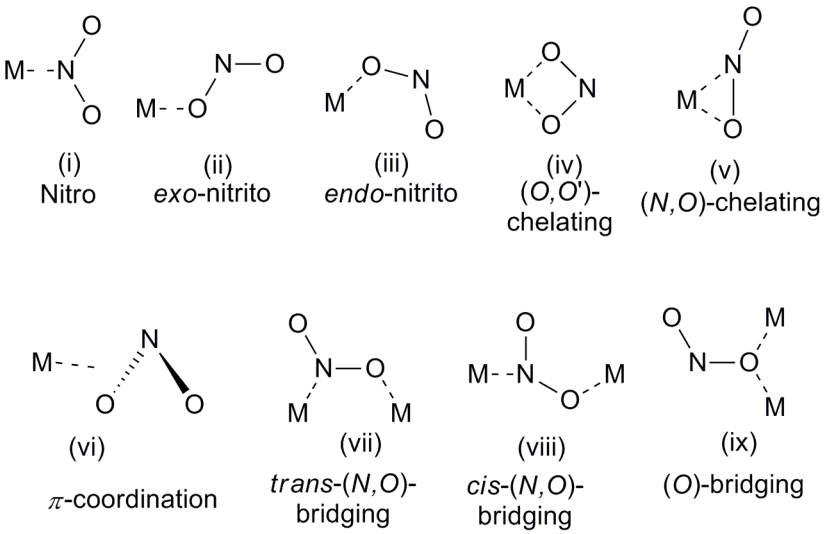

Fig. 1 The possible coordination modes of the NO_2 ligand to one or more metal centres

a second isomer is required. We have, therefore, been exploring the thermodynamic and kinetic factors that favor the photogeneration of linkage isomers with a view to establishing methods for effecting high conversion percentages from the ground state. Recently, we identified the first system that converts 100 % reversibly, in the crystalline state, upon irradiation with UV light (400 nm) to a linkage isomer at temperatures up to 160 K. The reversible conversion process for the nickel(II) complex, [Ni(dppe)(η^1-NO_2)Cl], to the η^1-*O*NO linkage isomer was established photocrystallographically and with solid state Raman spectroscopy.[15] Similarly, we have found that the complex [Ni(Et_4dien)(NO_2)$_2$] undergoes reversible nitro-nitrito linkage isomerism following exposure to either UV light or heat.[16] These results, coupled with the identification by Coppens of a novel photochemically-induced oxygen transfer within crystals of *cis*-[Ru(bpy)$_2$(NO)(NO_2)][PF_6]$_2$,[17] has led us to investigate other nitro-complexes in order to establish their solid state photochemical properties. The nitro-ligand is a well-known example of an ambidentate ligand and can adopt a range of coordination modes as illustrated in Figure 1.[18] The first four are the most common modes while modes (v) and (vi) have not yet been identified by X-ray diffraction studies. This means that, as has been seen in the previous photocrystallographic studies of metastable linkage isomers, there is scope for the identification of new species.

We now report our photocrystallographic and solid state Raman spectroscopy studies on three six-coordinate nickel(II) *trans*-di-nitro complexes stabilized by two bulky bidentate nitrogen donor ligands, [Ni(L)$_2$(η^1-NO_2)] (L = (1-(2-aminoethyl)piperidine) aep **1**, (1-(2-aminoethyl)morpholine) aem **2**, (1-(2-aminoethyl)pyrolidine) aepy **3**) (Chart 1) and their conversion to the equivalent nitrito linkage isomers **1†O**-**3†O** upon low temperature photoirradiation.

Experimental

Raman spectra were recorded on a confocal Horiba-Jobin-Yvon LabRAM Raman Microscope using a 660 nm diode laser and a 600 lines/mm grating. The detector was a Synapse CCD detector. The spectra shown were recorded using *ca.* 10 mW laser power. Temperature control was achieved using a Linkam FTIR600 variable-temperature stage with CaF_2 windows and modified tubing to fit the Raman spectrometer. Crystal irradiation was performed using a cluster of seven UV LEDs (400 nm) placed 8 mm above the sample.

X-ray diffraction investigations were carried out on Station 11.3.1 of The Advanced Light Source (ALS),[19] Lawrence Berkeley National Laboratory and on Station 9.8 of Daresbury Synchrotron Radiation Source.[20] Single-crystal X-ray data collections were carried out on Bruker APEXII CCD diffractometers equipped with either an Oxford Cryosystems cryostream cooling device[21] (for temperature studies in the range 90-300 K) or an Oxford Cryosystems N-Helix crystal cooling device[22] (for temperature studies in the range 30-90 K).

Suitable single crystals were mounted on the diffractometer and cooled to 100 K. Ground state structures ("dark") were collected with no external light. The crystals were then irradiated *in situ* using a ring of 6 LEDs.[23] Irradiation of the single crystals in different experiments was carried out using a range of LED wavelengths (UV: 400 nm, 350 mcd; blue: 470 nm, 3300 mcd; green: 525 nm, 7500 mcd and 600 nm, 1600 mcd). During the exposure the crystal was continuously rotated to maximize the uniformity of radiation. After exposure a second dataset ("light") was collected and the level of photo-activation conversion was assessed through structure solution and refined with the nitro and nitrito components being treated as a disorder model with the total occupancy of each atom being summed to unity. The process of irradiation, dataset collection, solving and refining of the crystal structure was repeated until the maximum level of conversion to the nitrito complex was achieved. The crystal structure was then measured at different temperatures in 10 K intervals between 30-150 K to assess the temperature range over which the metastable state was present. The optimum wavelength for

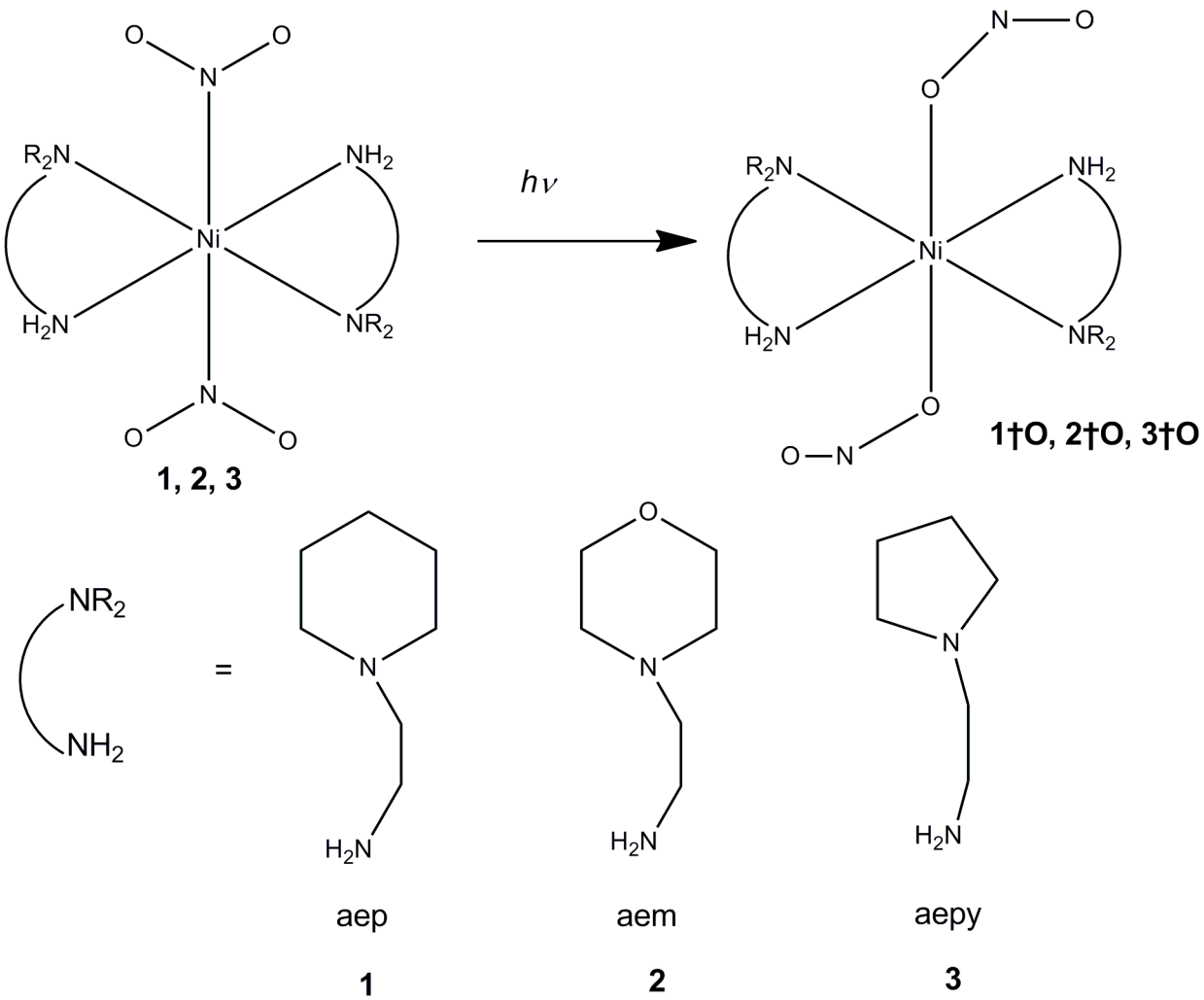

Chart 1

illumination was established by varying the excitation wavelength LEDs a temperature of 90 or 100 K.

The program APEX[24] was used for collecting frames, indexing reflection, and determination of lattice parameters and SADABS[25] for absorption correction. The structures were solved by direct methods using SHELXS-86[26] and refined by full-matrix least-squares on F^2 using SHELXL97.[27] Crystal data and refinement procedures are summaried in Table 1.

CCDC reference numbers 00000000 – 00000000.

See http://www.rsc.org/suppdata/dt/xx/xx/xxxxxxxx/ for crystallographic data in CIF or other electronic format.

The complexes **1**, **2** and **3** were synthesized, following literature methods.[28] In each case a methanolic solution (5 ml) of the diamine (2 mmol) was added to a methanolic suspension (10 ml) of potassium hexanitronickelate(II) monohydrate (1 mmol).[29] Crystals were obtained through slow evaporation of the solvent from the dark green solution.

Results and Discussion

At the outset, it was decided to undertake the initial experiments on *trans*-[Ni(aep)$_2$(NO$_2$)$_2$] since it was known that both the nitro **1** (purple) and nitrito isomers **4** (blue) could be synthesized and characterized in the solid state.[29] The nitrito isomer **4** was obtained by irradiating solutions of the nitro isomer and then crystallizing the reaction product. In the crystalline state this nitrito isomer **4** adopts an *exo*-conformation and crystallizes in the orthorhombic space group *Pbca*, whereas the nitro form **1** crystallizes in the monoclinic space group $P2_1/c$ with the nickel atom in both structures sitting on a crystallographic centre of symmetry. The nickel atom adopts a pseudo-octahedral coordination environment with two *trans*-nitrite ligands and two bidentate aep ligands, bound through the nitrogen centres as illustrated in Figure 2a. In the structure there is *ca.* 21 % disorder present involving the ethylene carbon atoms C(1) and C(2) and part of the ring. This disorder was modeled with partial occupancies for each atom to summed to unity.

The key question posed was whether or not the nitro form could be converted into the nitrito form in the solid state by photo-activation. A suitable single crystal of **1** was placed on a diffractometer and cooled to 90 K, in the dark, and a high resolution X-ray dataset was collected. The structure was subsequently solved and refined (Figure 2a) and found to be

Table 1 Crystal data and refinement parameters for **1, 1†, 2, 2†, 3** and **3†**

compound	**1**	**1†**	**2**	**2†**	**3**	**3†**
empirical formula	$C_{14}H_{32}N_6NiO_4$	$C_{14}H_{32}N_6NiO_4$	$C_{12}H_{28}N_6NiO_6$	$C_{12}H_{28}N_6NiO_6$	$C_{12}H_{28}N_6NiO_4$	$C_{12}H_{28}N_6Ni$
formula weight	407.17	407.17	411.11	411.11	379.11	379.11
T/K	90	90	100	100	100	100
wavelength / Å	0.7749	0.7749	0.68960	0.68960	0.68960	0.7749
crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	P-1	P-1	$P2_1/c$	$P2_1/c$
a/Å	9.629(5)	9.672(4)	7.172(5)	7.2136(13)	8.6169(5)	8.349(2)
b/Å	8.240(2)	8.366(4)	7.988(5)	7.9994(14)	8.5490(2)	8.646(2)
c/Å	11.804(2)	11.903(5)	8.330(5)	8.3000(14)	11.5680(7)	11.836(3)
α/°	90	90	94.306(5)	94.581(2)	90	90
β/°	109.03(2)	108.936(6)	112.642(5)	111.364(2)	104.008(1)	102.692(3)
γ/°	90	90	100.496(5)	101.278(2)	90	90
V/Å^3	885.4(5)	911.1(7)	427.5(5)	431.39(13)	826.83(8)	833.5(3)
Crystal size/mm	0.10, 0.08, 0.08	0.10, 0.08, 0.08	0.10, 0.08, 0.08	0.10, 0.08, 0.08	0.08, 0.05, 0.05	0.08, 0 0.05
level of activation	0	16	0	22	0	35
Z	2	2	1	1	2	2
D_c/g cm^{-3}	1.527	1.484	1.597	1.582	1.523	1.511
μ/mm^{-1}	1.129	1.097	1.179	1.168	1.203	1.193
$2\theta_{max}$	66.868	66.36	59.00	59.12	59.04	60.82
sinθ/λ	0.711	0.706	0.714	0.715	0.715	0.653
reflections collected	8708	13361	4890	4826	9220	9187
independent reflections, R_{int}	2609, 0.064	2778, 0.0649	2523, 0.0190	2533, 0.0185	2512, 0.0306	2505, 0.039
reflections observed (I> 2σ(I))	2277	2289	2437	2389	2247	1468
T_{min}/T_{max}	0.7673	0.8155	0.7551	0.7352	0.758026	0.7230
final R_1, wR_2 [I>2σ(I)]	0.0434, 0.1150	0.0459, 0.1066	0.0278, 0.0722	0.0439, 0.1179	0.0285, 0.0729	0.0613, 0.1
final R_1, wR_2 (all data)	0.0481, 0.1178	0.0567, 0.1121	0.0288, 0.0732	0.0467, 0.1193	0.0320, 0.0756	0.1055, 0.1

[a] The starred structure determinations indicate a crystal that contains both the ground state and metastable state components.

essentially identical to that reported previously, allowing for the difference in the temperature at which the data was measured.[29] While remaining on the diffractometer at 90 K, the crystal was irradiated using LEDs. The LEDs were then switched off and another high resolution data set collected using the same parameters as before. On the completion of structure refinement it was found that there had been partial conversion to the *endo*-nitrito isomer, as shown in Figure 2b. The irradiated crystal shows an increase in disorder of the ethylene chain atoms C(1) and C(2) (70:30) as well. It was found that a maximum conversion to **1†O** (the *endo*-O-bound nitrito isomer) of 16 % was obtained, if the crystal was irradiated for 4 h, at 90 K, with LEDs of 470 nm. Interestingly, the *endo*-form of the NO_2 group was obtained, with the O-N-O unit forming a *U*-shape as illustrated in Figure 2c and there was no change in space group from the ground state nitro structure **1** and a volume increase of only *ca*. 26 Å^3 (2.9 % volume increase) (Table 1). Thus the space group of **1†** differs from that reported for the *exo* or *Z* nitrito-form **4**, which crystallises in space group *Pbca*.[30] These differences in the observed configurations of the NO_2 group may be related to the fact that a smaller movement of the atoms is required to obtain the *endo*-form from the *N*-bound nitro group and to the kinetics of the solid state process. An analysis of the packing showed no significant voids in either the crystal structures of **1** or **1†**.

In order to definitively establish the existence of the metastable state, the crystal was kept in the dark for 4 h at 90

K, after which time the structure was recollected and the metastable state remained completely unchanged. However, after warming the crystal to temperatures above 110 K or cooling below 60 K, redetermination of the structure showed

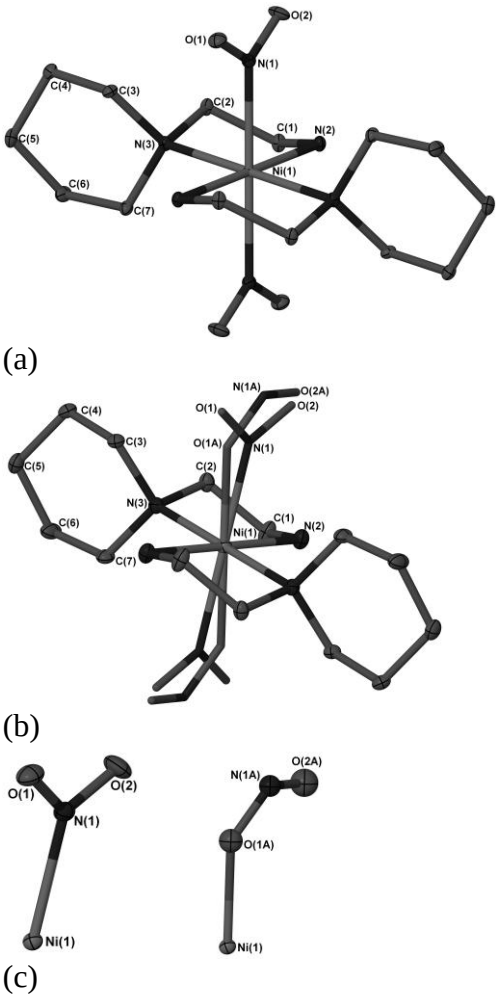

Fig. 2 a) Ground state structure of **1**. b) Photo-activated structure **1**† showing the remaining ground state and 16 % component of the metastable nitrito form. c) Close-up of the NO_2 group in **1**†, separated into the two components and confirming the presence of the *endo*-nitrito form. Where shown displacement ellipsoids are plotted on 30 % probability and hydrogen atoms and the disorder of the ethylene chain are eliminated for clarity.

that the metastable state completely converted back into the ground state. In addition, a subsequent re-determination of the structure, at 100 K, without illumination, was essentially identical to that obtained prior to irradiation with no evidence of the oxygen-bound isomer and with comparable ellipsoids to the initially determined ground state structure **1**.

In the photocrystallographic study of *cis*-$[Ru(bpy)_2(NO)(NO_2)][PF_6]_2$ the *endo*-configuration is observed at 200 K while the *exo*-conformation is present at 90 K.[17] To test if a similar behaviour could be found for our system a variable temperature study was undertaken. In experiments at temperatures between 60K and 120 K, a constant percentage conversion to the nitrito isomer was observed. Above 120 K and below 60 K no conversion was observable following irradiation of the crystal.

In order to corroborate the single crystal X-ray diffraction results a complementary series of solid-state Raman

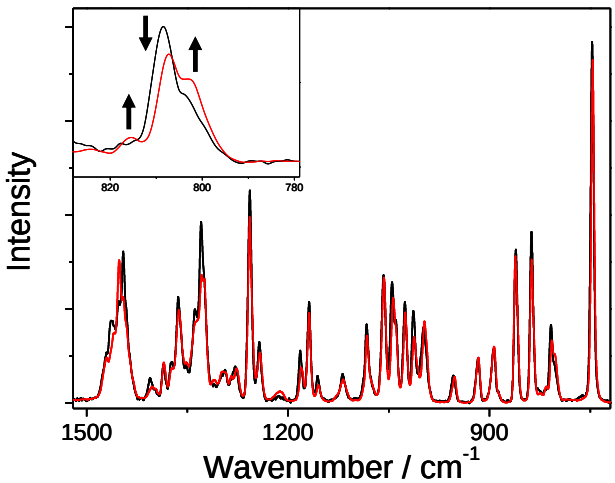

Fig. 3 . Solid state Raman spectra of **1** at 100 K recorded before photolysis (*black*) and after 4 hours UV LED photolysis (*red*). *Insert*: An expansion of the region around 810 cm^{-1}.

spectroscopic experiments were undertaken on $[Ni(aep)_2(\eta^1\text{-}NO_2)_2]$ **1**, $[Ni(aem)_2(\eta^1\text{-}NO_2)_2]$ **2** and $[Ni(aepy)_2(\eta^1\text{-}NO_2)_2]$ **3** to facilitate further single crystal X-ray photocrystallographic experiments. In each case, a single-crystal sample was cooled to 100 K and the Raman spectrum recorded. After photolysing the sample with UV LEDs, if necessary, the spectrum was re-recorded. Further spectra were measured then as the sample was warmed up in 10 ºC increments.

The ground state nitro-(η^1-NO_2) isomer has characteristic Raman bands, particularly the $\delta(NO_2)$ deformations in the 800-900 cm^{-1} region and the ν(N-O) stretches in the region 1350-1500 cm^{-1}.[15] The presence of two nitro groups results in splitting of the bands due to coupling. The ν(N-O) stretches are often overlapped with other Raman bands, making them less useful for assignment and since the $\delta(NO_2)$ deformations are less obscured we have used these bands to monitor interconversion of isomers within the crystal.

The Raman spectrum of **1** at 100 K is shown in Figure 3, along with the spectrum of the complex after irradiation for 4 hours with UV LEDs. The $\delta(NO_2)$ deformation band of the nitro isomer ground state at 808 cm^{-1} decreases in intensity and bands at 815 and 803 cm^{-1} are formed, corresponding to the partial formation of the nitrito isomer. The drop in intensity of the nitro-isomer ground-state band on photolysis is *ca*. 19 %, consistent with the 16 % conversion measured by crystallography.

Figure 4 shows the Raman spectra recorded in the $\delta(NO_2)$ region after photolysis of **1** as the temperature is subsequently increased from 100 K to 110, 120 and 130 K. The nitrito bands at 815 and 803 cm^{-1} decrease and the parent nitro band at 808 cm^{-1} grows in intensity as the temperature is increased. Between 110 K and 120 K the parent spectrum is almost completely recovered and by 130 K the nitrito isomer bands

have completely decayed. This agrees well with the observed metastable temperature of 110 K recorded by crystallographic measurements.

A photocrystallographic experiment was then performed on $[Ni(aem)_2(\eta^1\text{-}NO_2)_2]$ **2** using the same procedure as for **1**.

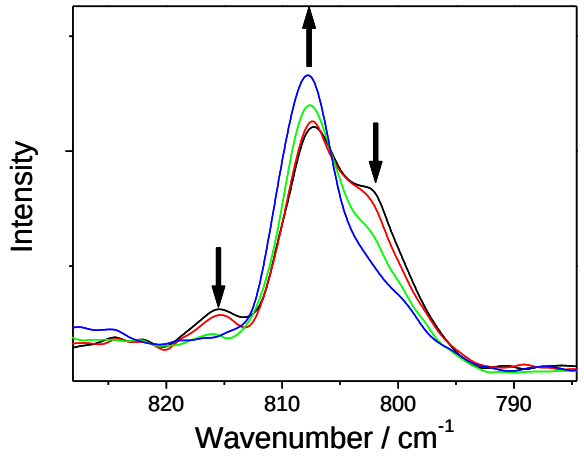

Fig. 4 Solid state Raman spectrum of **1** after 4 hours UV LED photolysis warmed from 100 K (*black*) to 110 K (*red*), 120 K (*green*) and 130 K (*blue*).

The ground state structure is illustrated in Figure 5. The complex crystallizes in the triclinic space group *P*-1, not *P*1 as reported in the initial paper[30] with the nickel atom sitting on the inversion centre. The coordination geometry around the nickel centre is octahedral with the two nitrite ligands in a *transoid* orientation. The photo-activated nitrito species is disordered over two positions on either side of the original ground state nitro configuration as shown in Figure 5b. Both species are *endo* coordinated and are populated to different levels (*ca*.1:3).

At 100 K under optimised conditions up to 22 % conversion was achieved after a period of 3 h by irradiation with blue light (wavelength 470 nm). The photo-activated structure is stable at low temperature in the dark and only converts back to the ground state above 120 K. It also exists at temperatures down to 30 K. The unit cell shows a slight and hardly significant increase upon irradiation. The change is only of 4 $Å^3$ or 0.9 vol. %. These changes involved an increase in both *a* and *b*, but a decrease in the *c* axis. There was also a slight increase in the α and γ angles and a decrease in β (Table 1).

The ground state Raman spectrum of **2** at 100 K is shown in Figure 6, along with the spectrum of the complex after being irradiated for 1.5 hours with UV LEDs. The $\delta(NO_2)$ deformation band of the nitro isomer ground state at 812 cm^{-1} decreases in intensity significantly and a new band at 821 cm^{-1} is formed, corresponding to formation of the nitrito isomer. Raman spectroscopy suggests that the conversion is complete, whereas the crystallographic experiment recorded a total conversion of 22 %. This discrepancy may be explained by partial decay of the photoinduced species in the Raman experiments due to local laser heating. This difference also highlights one of the challenges of these experiments, that is whether the irradiation process affords full penetration of the crystal.

Warming the crystal of **2**† after excitation resulted in the reformation of the ground state at temperatures above 130 K, in reasonable agreement with the crystallographic measurement of 120 K.

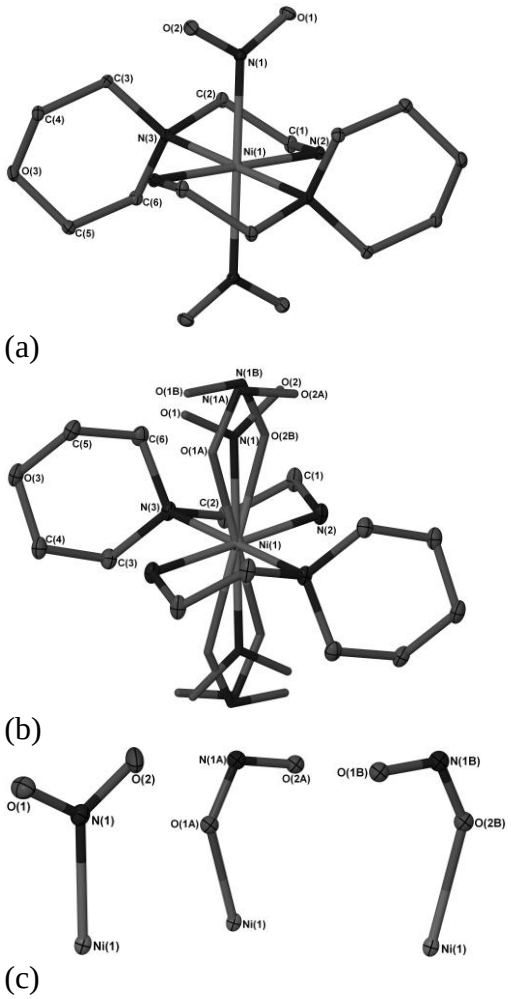

Fig. 5 a) Ground state structure of **2**. b) Photo-activated complex **2**†. c) Close-up of the NO_2 group in **2**†, separated into the three components. Where shown displacement ellipsoids are plotted on 30 % probability and hydrogen atoms have been removed for clarity.

The complex $[Ni(aepy)_2(\eta^1\text{-}NO_2)_2]$ **3** crystallized in the space group $P2_1/c$.[27] The coordination geometry around the nickel centre is similar to the one of complex **1**. Similar to the structure of **2**† the photo-activated nitrito species **2**†**O** occupies two different positions, although one is an *endo* and one an *exo* isomer, as shown in Figure 7. The major isomer (*endo*) accounts for up to 25% of the total 35% conversion at 100 K after 1 hour with green light. The increase of isomerisation of the nitrite group is followed by an appearance of disorder of the ethylene chain from 0% to a maximum of 35%. The photo-activated structure is stable at low temperature without further irradiation and converts back to the ground state above 120 K. The changes, which occur during irradiation, involve an increase of the unit cell volume

of around 7 Å^3, due to an increase in *b*, *c* and a decrease in *a* and *β*. The increase of the unit cell is of only 0.8 vol. %.

The ground state Raman spectrum of **3** at 100 K is shown in Figure 8 and contains several overlapping bands in the δ(NO_2) region of the spectrum consistent with significant coupling between the two NO_2 groups. This complex underwent

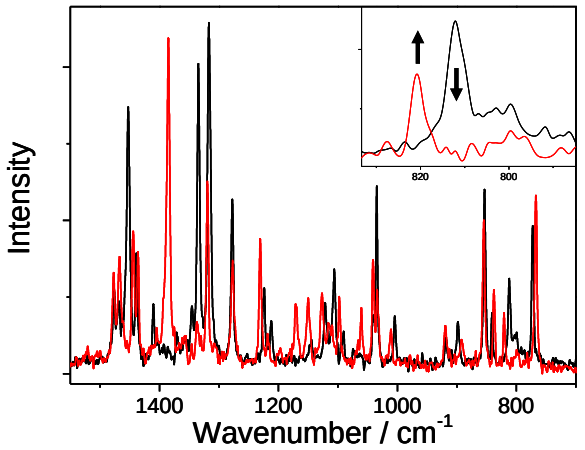

Fig. 6 Solid state Raman spectra of **2** at 100 K recorded before photolysis (*black*) and after 1.5 hours UV LED photolysis (*red*). *Insert*: An expansion of the region around 810 cm^{-1}.

photolysis readily on exposure to the 660 nm laser of the Raman spectrometer and the resulting spectrum also shown in Figure 8 was recorded after a total of 15 minutes irradiation. The δ(NO_2) deformation bands of the nitro isomer ground state appear to decrease around 804 cm^{-1} and new bands appear at 798 and 861 cm^{-1}. There are other changes in this region but the spectra are not of sufficient quality to resolve clearly these differences. The crystallographic experiment suggests that the complexity may be due to the presence of a mixture of photoproducts – both the *endo*- and *exo*-nitrito products. Another explanation could be that only one of the nitro groups is converted following irradiation which would result in lowering the symmetry of the molecule resulting in the Raman spectra being less easy to interpret. The overlap of the Raman bands also makes it difficult to estimate the percentage conversion and demonstrates the utility of the crystallographic experiment in directly quantifying the degree of photoinduced isomerism to the *endo*- and *exo*-forms.

As with **1†** and **2†**, warming the crystal of **3†** after excitation resulted in the reformation of the ground state at temperatures above 130 K, again a little higher than, but in reasonable agreement with the crystallographic measurement of 120 K.

Conclusions

Single crystal X-ray photocrystallographic and solid state Raman spectroscopy studies have shown that the metastable nitrito complexes [Ni(aep)$_2$(η^1-ONO)$_2$] **1†O**, [Ni(aem)$_2$(η^1-ONO)$_2$] **2†O** and [Ni(aepy)$_2$(η^1-ONO)$_2$] **3†O** are generated, with a maximum bulk conversion level of 35 %, at temperatures below 120 K, when crystalline samples are irradiated with appropriate LEDs. All three complexes adopt an *endo*-conformation of the nitrito group, but there is also crystallographic evidence for the presence of an *exo*-nitrite in the structure of **3†**. Thus, the structure of [Ni(aep)$_2$(η^1-ONO)$_2$] **1†O** contrasts with that of the same compound, **4**, prepared by the synthesis of the complex under irradiation in solution, followed by recrystallisation, where the ONO groups

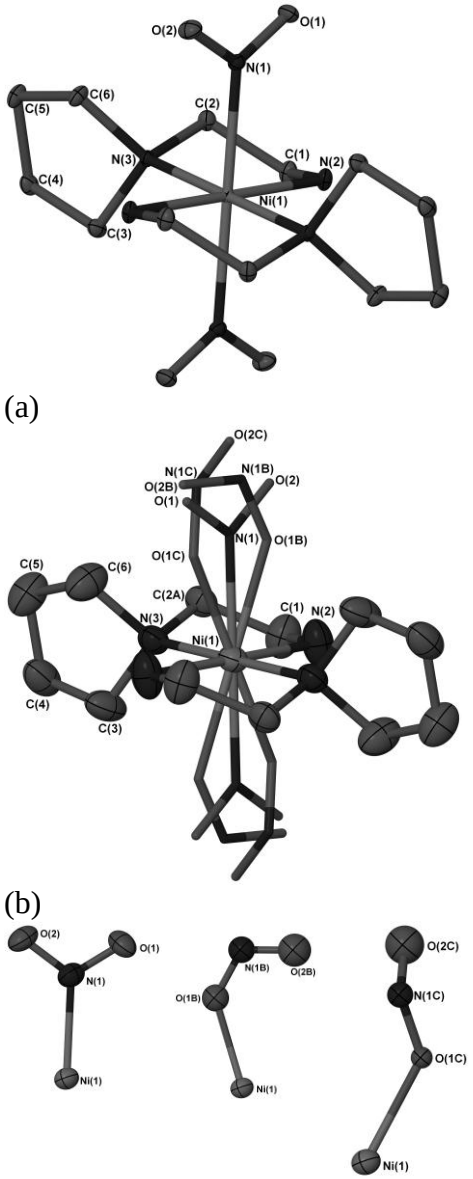

Fig. 7 a) Ground state structure of **3**. b) Photo-activated complex of **3†** with disorder of the ethylene chain eliminated for clarity. c) Close-up on the NO_2 group, separated into the three components. Where shown displacement ellipsoids are plotted with 30 % probability and hydrogen atoms have been removed for clarity. Because of the disorder in the system N-O distances in the low occupancy components are not reliably determined.

adopt *exo* configurations. While the metastable structures of **2†O** and **3†O** remained when the temperature was reduced to 30 K, for **1†**, at temperatures below 60 K, the metastable state was quenched and only a structure corresponding to the ground state nitro complex **1** was observed.

Of note is the small changes in unit cell dimensions upon isomerisation, with the unit cell for **1** to **1**† increasing in volume by 26 Å^3, **2** to **2**† by only 4 Å^3, and **3** to **3**† by only 7 Å^3. These volume changes are similar or smaller than the volume changes observed by Ohashi in his pioneering work of single-crystal to single-crystal transformations in several series of cobaloxime systems,[31] which suggests that the reaction cavity required for the isomerisation process to occur is small. There are certainly no identifyable voids in any of the nitro or nitrito structures that would correlate with the presence of larger reaction cavities.

The subtle differences in behaviour between these three closely related systems,[15,16] and other related nickel nitro complexes, are currently to subject of a detailed kinetic investigation.

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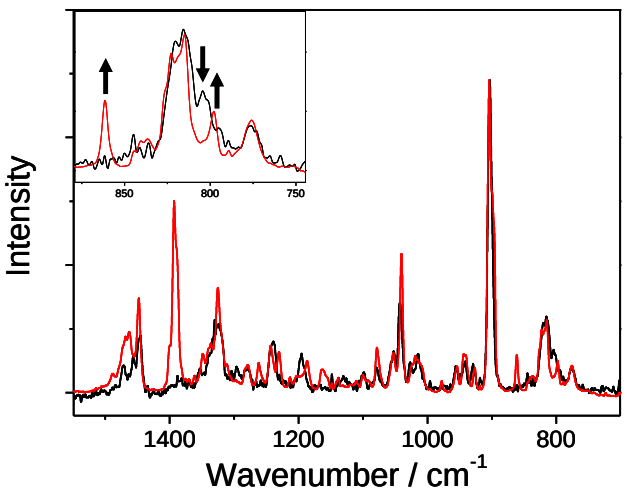

Fig. 8 Solid state Raman spectra of **3** at 100 K recorded before photolysis (*black*) and after photolysis (*red*). *Insert*: An expansion of the region around 810 cm^{-1}.

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Notes and references

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Graphical Abstract

Photocrystallographic Identification of Metastable Nitrito Linkage Isomers in a Series of Nickel(II) Complexes

S. K. Brayshaw, T. L. Easun, M. W. George, A. M. E. Griffin, A. L. Johnson, P. R. Raithby, T. L. Savarese, S. Schiffers, J. E. Warren, M. R. Warren, and S. J. Teat

Photocrystallographic and Raman experiments show that a series of Ni(II) di-nitro complexes undergo reversible linkage isomerism in the single-crystal.